VII.11 Novel Ceria-Based Materials for Low-Temperature SOFCs

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Objectives

- Develop single-phase cathodes, composite cathodes, and/or two-layer cathode structures that provide efficient low-temperature electrochemical performance and are adaptable to different solid oxide fuel cell (SOFC) materials systems and different SOFC cell/stack designs.
- Evaluate the effects of composition and synthesis conditions on thermal expansion and high-temperature electrical conductivity of perovskite electrode powders in the B-site doped lanthanum strontium ferrite (LSXF) system.
- Evaluate the effects of composition of LSXF perovskite materials on their high-temperature reactivity with electrolyte materials (yttria-stabilized zirconia, YSZ, and gadolinium-doped ceria, GDC) that are being considered for low-temperature solid oxide fuel cells.
- Evaluate the effects of composition, thickness and morphology on sheet resistance and area specific resistance of screen-printed coatings of LSXF perovskite and LSXF/GDC composite cathode materials, and correlate results with characterization data.

Approach

- Synthesize and characterize a matrix of single-phase electrode (LSXF) powders selected for their low-temperature electrochemical performance in SOFC systems.
- Measure high-temperature electrical conductivity and evaluate interfacial resistance of the single-phase LSXF materials.
- Synthesize and characterize a matrix of composite cathode (LSXF/GDC) powders to further improve low-temperature electrochemical performance of SOFCs.
- Measure high-temperature electrical conductivity and evaluate interfacial resistance of the composite cathode materials.
- Prepare fuel cell samples with most promising cathode materials and test their performance at low operating temperatures (YSZ-based cells at 600-850°C and GDC-based cells at 500-700°C).

Accomplishments

- Synthesized and characterized over 30 highly conductive single-phase cathode materials.
- Developed and characterized composite cathode materials based on above analysis.
- Demonstrated improved performance of the composite cathode materials over the single-phase materials.

Future Directions

- Evaluate interfacial resistance of other LSXF cathode materials from the characterized set in composite cathode form.
- Analyze interfacial resistance of composite cathode materials with different LSXF:GDC ratios.
- Demonstrate SOFC performance on ceria- and zirconia-based cells.

Introduction

We have investigated several new single-phase cathodes and composite cathode materials with the goal to reduce the interfacial resistance between the cathode and the electrolyte. We have evaluated the effect of processing route and composite electrolyte component characteristics on the interfacial resistance. The initial analyses determined that the composite cathode materials outperform the single-phase lanthanum strontium ferrite (LSF) and B-site doped LSF materials.

Approach

LSXF perovskite system was identified as having promising electrochemical performance, and a set of LSXF compositions was synthesized and characterized for phase purity and conductivity. Upon evaluation of the single-phase materials, the most promising material was selected for study in the composite form with GDC powders. The study of the composite materials focused on determining the surface area effect on the electrochemical performance of the cathode. The composites were prepared by milling LSXF powder with two different GDC powders, with high and low specific surface area (SSA), at LSXF:GDC volume ratio of 60:40. The composites were made into inks and screen printed symmetrically onto two faces of GDC and YSZ electrolyte discs. The interfacial resistance was analyzed using a Solartron SI 1260 Impedance Analyzer.

Results

In previous work in this system, the LSXF compositions have been evaluated and found to have excellent performance on GDC electrolytes. Demonstration of low area specific resistances is shown in Figure 1. These bulk resistances of symmetric sandwich cells have been very low for a number of compositions at temperatures above 600°C.

In this phase of the study, a number of LSF-based cathodes have been evaluated in contact with YSZ to determine processing parameters and composite fabrication processes that provide the best interfacial resistance behavior. LSF-40 was selected for

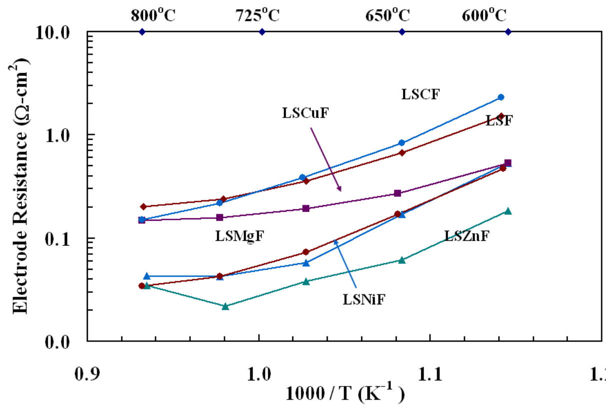

Figure 1. Interfacial resistance data for LSXF materials on GDC electrolyte substrates measured by DC resistance on symmetric samples. The resistance of the GDC electrolyte has been subtracted from the data.

evaluation of its performance versus processing technique. LSF-40 was prepared by three different techniques. The oxide and carbonate forms of lanthanum, strontium, and iron were milled together and calcined at 1300°C to ensure formation of single-phase perovskite. The calcined powders were then either attrition milled for one to six hours or ball milled for 12 hours. The three milling techniques allowed for evaluation of the powder at different surface area values. The ball-milled powder achieved surface area of 2.776 m^2/g; the attrition-milled powder achieved surface area of 3.423 and 7.700 m^2/g for one- and six-hour milling time, respectively. Each powder was made into an ink. The inks were screen printed and annealed on YSZ disks. The annealing temperature for the ball-milled powder was 1050°C. The attrition-milled powders were annealed at 1050°C and 1000°C for one- and six-hours milling time, respectively. The samples were then tested for interfacial resistance using 1260 Impedance Analyzer. Figure 2 shows the impedance spectra for the three LSF-40 powders measured at 600°C. The data shows that the interfacial resistance decreases with the increasing surface area and decreasing adhesion temperature. The reason for this trend could be explained by the formation of resistive phase at the interface of cathode and electrolyte. The lanthanum- and praseodymium-containing materials have a tendency to form pyrochlore compounds with ZrO_2 such as $La_2Zr_2O_7$, which is highly resistive.

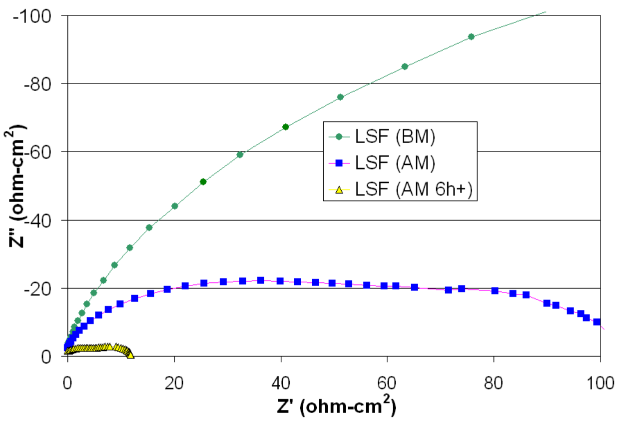

Figure 2. Interfacial resistance data for LSF-40 processed by either ball milling or attrition milling for one and six hours measured on YSZ electrolyte substrates at 600°C.

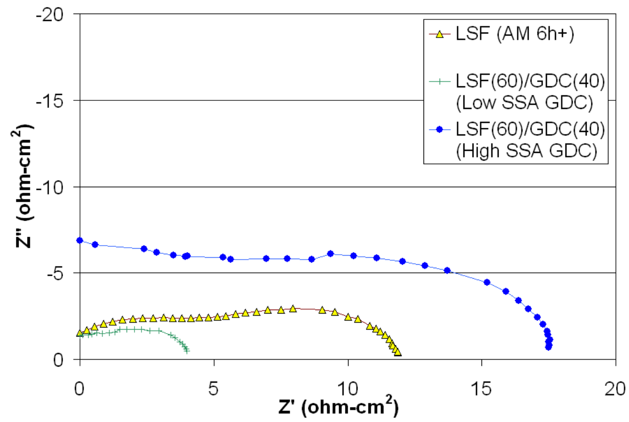

Figure 3. Interfacial resistance data for LSF-40 and composite cathode materials made with two different surface area GDC powders measured on YSZ electrolyte substrates at 600°C.

The probability of reaction between YSZ substrate and cathode materials increases with higher annealing temperature. The high surface area powder adheres to the YSZ substrate at lower temperature; hence, the pyrochlore materials are not formed at the interface and the interfacial resistance is low.

LSF-40 attrition milled for six hours was used to evaluate composite cathode materials with GDC as the electrolyte component of the composite. Two GDC powders were mixed with LSF-40: a nano-scale material with surface area of >100 m^2/g (high SSA) and a ceramic grade material with surface area of <10 m^2/g (low SSA). The composite powders were mixed at 60:40 ratio of LSF:GDC. The powders were then calcined to achieve surface area similar to the pure LSF-40 (7.700 m^2/g). Upon calcination, the composite with high-SSA GDC achieved surface area of 7.572 m^2/g, and the composite with low-SSA GDC achieved surface area of 7.619 m^2/g. Each powder was made into an ink. The inks were screen printed and annealed on YSZ disks. The samples were adhered at 1000°C. The interfacial resistance of the samples was measured at 600°C. Figure 3 shows the impedance spectra for the LSF-40 and the composite powders.

The data shows that the performance of the cathode can be improved by addition of the electrolyte material such as GDC to the pure perovskite powder. However, it is essential that components of the composite are carefully selected based on their initial surface area. The impedance results show that the high-SSA GDC composite cathode has higher interfacial resistance, while the low-SSA GDC composite cathode has a lower interfacial resistance than the pure LSF-40 material. The low SSA-GDC composite cathode showed an improvement over the LSF-40 powder by increasing the triple point boundary area of the cathode. However, in the case of the high-SSA GDC composite cathode, it is believed that due to the extreme difference in surface area between the LSF-40 and nano-scale GDC materials, the particles of LSF were completely covered by the fine GDC powder, in effect decreasing the overall triple point boundary area of the cathode.

Conclusions

- Within the evaluated set of single-phase materials, LSF-40 achieved the highest conductivity, while PSF-40 appears to have the lowest interfacial resistance.
- The processing technique of the cathode powders is an important factor in cathode performance. Higher surface area powders lead to lower adhesion temperatures and lower interfacial resistance.
- LSF/GDC cathode composites outperform single-phase LSF material when the surface area of the components is carefully taken into consideration.